International Journal of Trend in Scientific Research and Development (IJTSRD)
Volume 4 Issue 4, June 2020 Available Online: www.ijtsrd.com e-ISSN: 2456 – 6470

Corrosion Inhibition of Mild Steel in HCl Medium by a Condensation Product

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ABSTRACT

A condensation product (CP) was successfully synthesized from reaction of dimethyl amino benzaldehyde and aniline giving yields of 80%. The compound was characterized by Fourier Transform Infrared (FTIR) Spectroscopy. The corrosion inhibiting property of the CP on mild steel in HCl solution were investigated by the weight loss measurements, electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LPR). The concentrations of CP were varied from 1 x 10^{-3} M to 5 x 10^{-3} M. The inhibition efficiencies obtained from all the methods employed were in good agreement where the percentage of inhibition efficiencies increased with concentration of CP. Results showed that CP was the better inhibitor with inhibition efficiency of 90% at 5 x 10^{-3} M additive concentration. This is likely due to the effect of its large molecular size, higher number of electroactive heteroatoms and bigger π-electron cloud of the conjugated double bond system.

KEYWORDS: *condensation product, Corrosion inhibitor, Hydrochloric acid, Mild steel*

How to cite this paper: Ganesha Achary "Corrosion Inhibition of Mild Steel in HCl Medium by a Condensation Product" Published in International Journal of Trend in Scientific Research and Development (ijtsrd), ISSN: 2456-6470, Volume-4 | Issue-4, June 2020, pp.84-88, URL: www.ijtsrd.com/papers/ijtsrd30869.pdf

IJTSRD30869

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I. INTRODUCTION

The increase in industrialization has lead to the consumption of more and more metals and nonmetals under different conditions in assorted parts of life. Corrosion of metal is the degradation of materials by electro chemical reactions. The investigation of corrosion inhibition of mild steel in hydrochloric acid is a subject of practical interest as it is commonly used in many engineering applications [1, 2]. Organic compounds containing electro active functional groups and π electron systems are usually good inhibitors of corrosion for many metals and alloys in corrosive environment. They do so by adsorption and this is often largely a function of their molecular structure. Those inhibitors containing oxygen, sulpher or nitrogen are generally most effective [3].

Heterocyclic compounds with various substituents are considered to be the effective corrosion inhibitors for metals in acid media. Schiff bases and condensation product molecule is reasonably a good corrosion inhibitor due to the presence of nitrogen atom as well as an imine functional group and are important class of ligands in coordination chemistry and find extensive applications in different fields [4-8].

Compounds containing π bonds and lone electron pairs generally exhibit good inhibitive properties as they can facilitate effective adsorption through their interaction with the vacant d-orbitals of metal atoms [9, 10]. Several studies reported that the inhibition efficiency of a Schiff base was much greater than its precursor molecules due to the presence of -C=N- group(s) in the molecule. Their effectiveness is also related to the chemical composition, molecular structure and their affinities for the metal surface [11, 12].

The aim of the present work is to prepare a condensation product then to study the corrosion behavior of mild steel in hydrochloric acid in absence and presence of a this condensation product.

II. EXPERIMENTAL

Materials

All chemicals Aniline, 4- dimethylaminobenzaldehyde, HCl (SD Fine), and ethanol used in this work were laboratory pure. All organic solvents were obtained as pure grade materials. Mild steel strips with chemical composition (C-1.14%, Mn-0.2%, P-0.10%, S-0.03% Cr-0.01% and Fe-98.52%) were used for electrochemical measurements. Mild steel sheets having a size 7×3×0.4 cm were used. For electrochemical studies, same coupons having 1 cm^2 area were used. All specimens were cleaned using the procedure of ASTM standard G1-82. All tests were performed at room temperature. The inhibitor concentrations chosen were 1-5×10^{-3}M in HCl.

Synthesis of Condensation product (CP):

The condensation product was synthesized by mixing ethanolic solution of 4-dimethyl amino benzaldehyde and aniline in 1:1 mole ratio in a 250 mL two necked round bottomed flask equipped with a magnetic stirrer, condenser

and a thermometer. Few drops of concentrated HCl were added to catalyze the reaction The reaction mixture was heated to 60-70°C for 4h and then the formed precipitate was filtered, washed several times and dried in a desiccators over calcium hydroxide.

Characterization of condensation product:

The products were purified and its structure was confirmed by (FTIR) spectroscopy and elemental analysis. FT-IR spectra of the compound was recorded on a Shimadzu-FTIR-8400S Spectrometer in a range of 4000-400 cm^{-1} using KBr pellets. The chemical structure of the prepared compound is confirmed by the FTIR spectroscopy. The band at 1585.6 cm^{-1} and 3070 cm^{-1} represents -CH=N-and ArCH respectively. The band at 1624 cm^{-1} was corresponded to the stretching vibration of C=O and that at 1150 cm^{-1} was the vibration of C-N. The band at 1381 cm^{-1} was the absorption of C-O, and that at 1014 cm^{-1} was ascribed to the -CH group. The band at 1501 ascribed to the C=C group. However, the bands at the band at 2920 cm^{-1} was attributed to - CH_2.

Weight loss measurements

Weight loss measurements were carried out in a glass cell. The test specimens were used in the form of sheets of dimensions 7×3×0.4 cm, the specimens were first mechanically polished by sequence of grinding with emery paper from 320 to 1200 grit to obtain a smooth surface, mirror finish and degreased with acetone, then washed with double distilled water, and finally dried between two filter papers and weighed. The test specimens were suspended by suiTableglass hooks at the edge of the basin containing 0.1, 0.2 and 0.3 M acid solution, and under the surface of the test solution by about 1cm.

After specified time of immersion specimens were taken out of the test solution, then rinsed with distilled water, dried as before and weighed again in the absence and presence of inhibitor. The average weight loss at a certain time for each set of three samples was taken in mg cm^{-2} and recorded. All experimental were carried out at 25, 50 and 75 ± 1°C. The percent inhibition efficiency was calculated using the following relationship.

$$\%IE = \frac{W_o - W}{W_o} \times 100$$

Where W_o and W are the weight-losses in the absence and presence of inhibitor.

Electrochemical Techniques

Galvanostatic Polarization studies:

For polarization study, mild steel specimens were immersed in 100 ml HCl solution without and with the condensation product. The test cell includes the metal specimen as a working electrode, corrosive solution in which the specimen was to be tested and saturated calomel electrode (SCE) as a reference electrode as well as Platinum electrode as an auxiliary electrode. The polarization study was made by using the above electrodes in a conventional three compartment cell and a DC power supply (Tektronix 36B). Polarization curves were plotted with potential against log current density (called Tafel plots). Cathodic and anodic polarization curves give cathodic and anodic Tafel lines correspondingly. The intersect point of cathodic and anodic Tafel lines gives the corrosion current (I_{corr}) and the corrosion potential (E_{corr}) [13]. The percentage inhibition efficiency %IE was calculated using the relationship,

$$\%IE = \frac{I^{o}_{corr} - I_{corr}}{I^{o}_{corr}} \times 100$$

Where I^{o}_{corr} and I_{corr} are the weight-losses in the absence and presence of inhibitor.

The electrochemical impedance spectra (EIS) studies:

The electrochemical impedance spectra of mild steel in absence and presence of various concentrations of inhibitors at 30°C is presented as Nyquist plot. The experimental data and calculated inhibition efficiency are summarized. The %IE at different concentration of each inhibitor in 1M HCl were calculated from the corresponding electrochemical impedance data according to equation. Where R_{ct} and R_{ct}^{I} are the charge transfer resistances in the presence and ct absence of inhibitors. It is evident from these plots that the impedance response of zinc has significantly altered after the addition of inhibitors to the corrosive solutions. The R_P values were used to calculate the inhibition efficiencies, using the relation,

$$\%IE = \frac{R_p - R_p^I}{R_p^I} \times 100$$

To study the effect of temperature on corrosion of mild steel in 1M HCl, the specimens were immersed in 100 ml of corrosive solution and corrosion loss was determined at solution at temperature for an immersion period of 2 h with and without inhibitors.

III. RESULTS AND DISCUSSION

Weight loss measurements:

Table1 shows the variation of weight-loss and inhibition efficiencies (%IE) with the concentrations of CP. The weight loss decreased with increasing CP concentration. The maximum inhibition efficiency, of 93% was observed at 5×10^{-3}M of CP and no change in %IE occurred above this concentration.

The protection efficiency (%IE) decreased with increase in acid concentration. This may be attributed to the increased hydrogen evolution and consequent stripping of the adsorbed compound from the metal surface [14]. Table2 presents the influence of acid and CP concentration on %IE. For a given strength of CP, %IE decreased slightly with acid strength. But for the same acid strength the %IE were directly depended on CP concentration.

Table1. Corrosion inhibition efficiencies by weight-loss method in 1 M HCl

Inhibitor Concentration (M)	Duration of immersion=1 hour		Duration of immersion=2 hour	
	Weight loss (g)	Percentage inhibition effiency, %IE	Weight loss (g)	Percentage inhibition effiency, %IE
Blank	0.0232	---	0.0176	-----
1×10^{-3}	0.126×10^{-3}	34.93	6.5×10^{-3}	63.07
2×10^{-3}	8.7×10^{-3}	55.06	5.2×10^{-3}	70.46
3×10^{-3}	6.9×10^{-3}	64.37	4.8×10^{-3}	72.73
4×10^{-3}	5.5×10^{-3}	78.59	2.8×10^{-3}	84.09
5×10^{-3}	5.1×10^{-3}	78.01	1.2×10^{-3}	93.08

Table2. Corrosion inhibition efficiencies by weight-loss method in 2 M HCl

Inhibitor Concentration (M)	Durationof immersion=1 hour		Durationof immersion=2 hour	
	Weight loss (g)	Percentage inhibition effiency, %IE	Weight loss (g)	Percentage inhibition effiency, %IE
Blank	0.011	---	0.0206	-----
1×10^{-3}	7.2×10^{-3}	34.50	9.9×10^{-3}	51.90
2×10^{-3}	6.3×10^{-3}	43.40	9.1×10^{-3}	55.82
3×10^{-3}	5.0×10^{-3}	54.54	8.3×10^{-3}	59.71
4×10^{-3}	4.5×10^{-3}	59.08	7.1×10^{-3}	65.57
5×10^{-3}	3.4×10^{-3}	69.09	2.61×10^{-3}	87.33

Galvanostatic Polarization studies:

Galvanostatic polarization measurements have been carried out to pool information concerning the kinetics of anodic and cathodic reactions. The polarization curves for mild steel in 1M hydrochloric acid solution in the absence and presence of various concentrations of the inhibitor molecules are shown in Fig.1. The values of electrochemical kinetic parameters, like corrosion current density (I_{corr}), corrosion current (I_{corr}), corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (b_a and b_c) and percentage inhibition efficiency (%IE), determined from these graphs by extrapolation method are listed in Table3. From the Tafel slopes, it clear that the corrosion inhibition efficiency is higher in the presence of CP. The I_{corr} values decreased significantly with increase in CP concentration. The corrosion potential (E_{corr}) shifted in the more positive direction in the presence of additive.

Table-3 Polarization parameters for mild steel electrode in 1 M HCl in the presence of different concentrations of CP

Concentration (M)	β_a (mV/dec)	β_c (mV/dec)	$-E_{corr}$ (mV)	i_{corr} (µA/cm²)	Inhibition efficiency (%)
Blank	83.0	92.2	545.0	230.5	--
1×10^{-3}	52.8	46.5	520.0	55.0	76.13
3×10^{-3}	60.7	54.5	518.0	43.5	81.12
5×10^{-3}	26.6	40.1	517.0	21.0	91.20

Inspection of Fig.1 shows that the addition of CP has an inhibitive effect on both anodic and cathodic parts of the polarization curves and shifts both the anodic and cathodic curves to lower current densities. This may be ascribed to adsorption of the inhibitor over the metal surface. Therefore, CP can be considered as a mixed type inhibitor,-which implies that the corrosion protection is mainly due to interaction of CP by simple blocking of the active sites of the metal surface.

The adsorption of compound leads to the formation of a surface film and thus provides a barrier between metal and acid [15]. This indicates that the compound is a good surface modifier for the corrosion protection of steel in HCl medium.

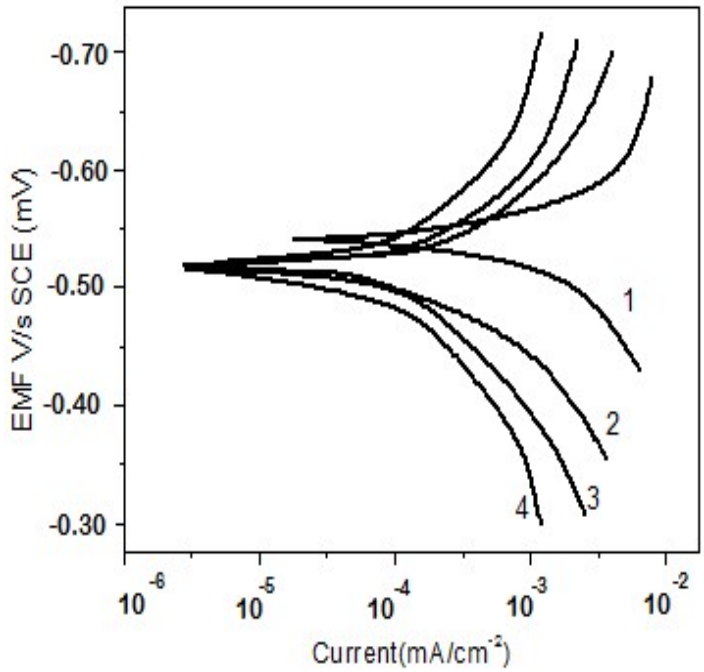


Fig.1. Polarization behavior of steel in 1M HCl with the addition of various concentrations of CP (Curves 1, 2, 3 and 4 represents Blank, 1, 3 and 5×10^{-3} M CP).

The electrochemical impedance spectra (EIS) studies:

The corrosion behaviors of carbon steel in 1 M HCl in the presence and absence of the synthesized inhibitors were investigated using EIS at 25°C. Fig.2 show that the Nyquist plots of mild steel in 1 M HCl solution with and without various concentrations of inhibitors.

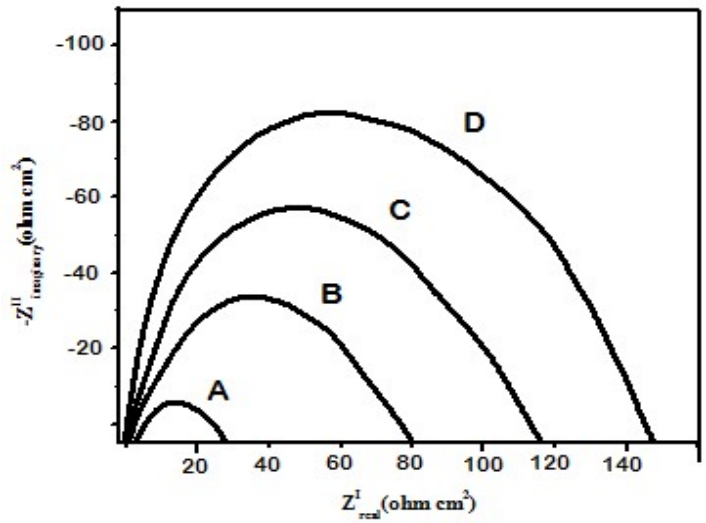


Fig.2: Nyquist plots for the mild steel in 1M HCl in the absence and presence of different concentrations of compound CP.

It is clear from these plots that the impedance response of mild steel has significantly changed after addition of the synthesized inhibitors in the corrosive media. This indicates that the impedance of an inhibited substrate increases with increasing concentration of inhibitor in 1 M HCl.

Table-3 Impedance parameters for mild steel electrode in 1M HCl in the presence of different concentrations of CP

Concentration (M)	Solution Resistance R_s(Ω cm^{-2})	Polarization Resistance R_p(Ω cm^{-2})	Inhibition efficiency (%)
Blank	0.13	26.2	
1×10^{-3}	0.20	80.0	67.25
2×10^{-3}	0.18	118.1	77.81
3×10^{-3}	0.22	155.5	85.15
5×10^{-3}	0.19	262.1	90.00

Various impedance parameters such as solution resistance (R_s), polarization resistance (R_p) and inhibition efficiency were calculated and listed in Table3. The Table3 illustrates the R_p values increase, with the inhibitor concentration increment and hence the inhibition efficiency increases and reaches 90% at 5mM concentration of the inhibitor. This increase in the efficiency of inhibition may be due to an increase in the surface coverage of inhibitor or may be due to the increase in the thickness of the electrical double layer, which suggests that, the inhibitor molecules act by adsorption at the metal/solution interface [16].

Adsorption isotherm

Adsorption isotherm can explain the adsorptive behavior of a corrosion inhibitor where it provides important information on the nature of the metal-inhibitor interaction. Several adsorption isotherms were tested for the description of adsorption behavior of studied compounds and it was found to obey the Langmuir adsorption isotherm. The surface coverage, θ, for various concentrations of the inhibitor was been calculated and the plot of C/θ vs. C, which gives straight lines as shown in Fig.3. The strong correlation (R^2 =0.9946) confirms the validity of this approach. Experimental results are in good agreement with Langmuir adsorption isotherm shown in the following equation;

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$

where C_{inh} is the inhibitor concentration and K_{ads} is the adsorption equilibrium constant.

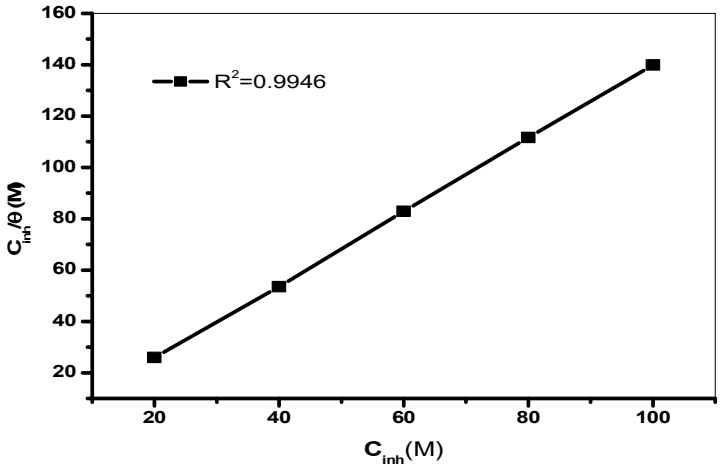


Fig.3. Langmuir plots for CP on mild steel in 1 M HCl

The value of K_{ads} is found to be 14.5 x 10^3. The increasing value of Kads shows increasing adsorption capability of the inhibitor on metal surface [17]. The K_{ads} is also related to the standard free energy of adsorption (ΔG_{ads}) according to the equation;

$$K_{ads} = \frac{1}{55.5} exp\left(\frac{-\Delta G_{ads}}{RT}\right)$$

where R is the universal gas constant (J mol^{-1} K^{-1}), T the absolute temperature (K) and 55.5 the value for molar concentration of water in solution (mol L^{-1}).

The values obtained were -35.8 kJ/mol for the inhibitor and the decreasing value of ΔG_{ads} indicates the increasing adsorption capability and the negative values show spontaneous adsorption of inhibitor molecule on metal surface.

The inhibition of active dissolution of metal in acidic media is due to the adsorption of inhibitor on metal surface forming protective layers through electron transfer from adsorbed species to vacant orbitals of low energy in metal to form coordinate type link [18]. The more efficient adsorption of inhibitor is attributed to the increase in electron density from the presence of N and O atoms, heterocyclic and aromatic ring that form effective adsorption on the metal surface.

IV. CONCLUSION

The condensation product was successfully synthesized and characterized. Corrosion inhibition investigations showed that the corrosion rate was found to be decreased with an increase in CP concentration and the compound display inhibitor properties. The presence of hetero atoms and π electrons affected more surface coverage on mild steel and higher electron density that promoted efficient adsorption of the inhibitor on mild steel. The Tafel plots showed that the compounds act as a mixed type of inhibitor. Polarization resistance values of solution with the inhibitor molecules obtained from EIS spectra were found to be increasing with increasing inhibitor concentration. The adsorption of the molecule on mild steel surface followed Langmuir isotherm at room temperature at all the concentrations studied. The inhibitor molecules adsorbed on the metal surface blocking the active sites. Higher surface coverage on the metal surface was obtained with higher inhibitor concentrations.

Acknowledgment

The author sincerely acknowledge the I. D. S. G. Government College for providing laboratory facilities for carrying out the above work.

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